

# Characterization of 2,6-Diamino-3,5-Dinitropyrazine-1-Oxide (LLM-105) as an Insensitive High Explosive Material

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# **Characterization of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) as an insensitive high explosive material**

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## **Abstract**

LLM-105 (2,6-diamino-3,5-dinitropyrazine-1-oxide) is a new molecule which has performance and insensitivity between those of HMX and TATB. Its calculated energy content is about 85% that of HMX and 15% more than that of TATB. It is thermally stable, insensitive to shock, spark and friction and has impact insensitivity level approaching that of TATB. These combined properties make it a realistic high-performance IHE material, attractive for applications that require moderate performance and insensitivity.

Several morphologies of LLM-105 and plastic-bonded formulations containing these materials and another binder were prepared and characterized. Their physical properties and detonation spreading characteristics are compared to those of ultrafine TATB. The impact sensitivity (drop hammer results) is sensitive to particle morphologies. Detonation-spreading, spot-size tests on LLM-105 compositions showed higher energy output and superior divergence behavior than is observed for ultrafine TATB. The small-scale safety data, pressing characteristics and results from divergence experiments will be summarized.

## **Introduction**

LLM-105 (2,6-diamino-3,5-dinitropyrazine-1-oxide) is a new molecule synthesized as part of our effort (1) to produce insensitive energetic materials that approach the energy of HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane). LLM-105 (Figure 1) is a dense molecule ( $\rho = 1.913$  g/cc) with excellent physical properties, good safety characteristics and 30% more energy than TNT. Differential scanning calorimetric traces (exothermic onset = 354°C) indicated that it is more thermally stable than most known HE and is nearly identical to TATB. It is insensitive to

spark and friction and has impact insensitivity ( $D_{h50} = 117$  cm) approaching that of TATB ( $> 177$  cm). Shock-loading tests, cook-off and cylinder experiments (2) show that this molecule exhibits explosive power between that of HMX and TATB. Cheetah calculations and experimental data (1, 3) have shown that this new molecule has about 20% more energy than TATB and about 81% that of HMX. These combined properties make LLM-105 a realistic high-performance IHE material, attractive for applications that require moderate performance and insensitivity.

The LLM-105 particle morphology and chemical purity are dependent on its synthetic and processing history. Collaborative development between synthesis and characterization efforts have yielded several materials with a range of particle sizes and morphologies. Pure LLM-105 and plastic bonded composites containing it and an inert binder have a range of safety and processing characteristics. Table 1 lists five types of LLM-105 particles that are available for study. Table 2 shows several plastic bonded formulations and their pressing characteristics.

Current interest has been on alternative IHE booster materials with energy approaching that of HMX. One type of LLM-105 (Type 3 in Table 1) was studied extensively. Its physical morphologies most resembles that of ultra-fine TATB (UF-TATB), i.e., granular shapes with low aspect ratio and some fines. The small-scale safety data and processing characteristics have been obtained. The detonation-spreading, spot-size (Floret) test, developed by Lee and co-workers (4), was selected as the primary performance test to screen the material's initiability and divergence behavior. The data are useful as quick feedback to synthetic chemists and processing engineers so that particle morphologies and formulations can be tailored for a specific application.

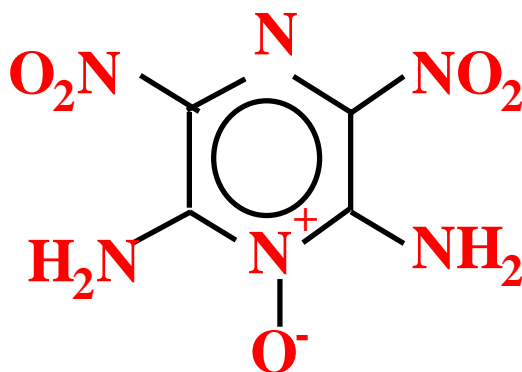


Figure 1: **LLM-105** (2,6-diamino-3,5-dinitropyrazine-1-oxide)

## Experimental

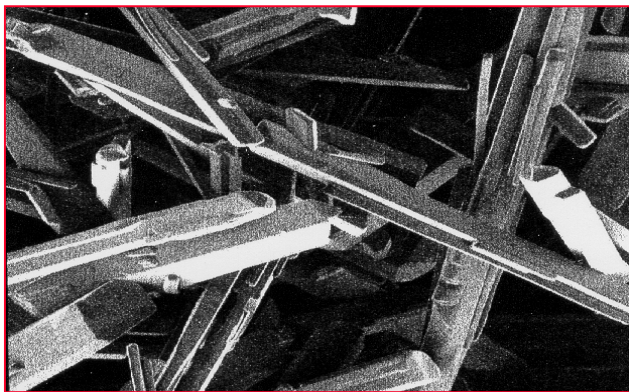
*Particle Morphology* - The synthesis and recrystallization process affect the LLM-105 particle purity and morphologies. There are five types of morphologies that have been produced (Table 1). Figure 2 shows the scanning electron micrographs (SEM) of several types. Figure 3 shows the particle size distributions for selected materials.

Table 1. Summary of several LLM-105 particles and selected data

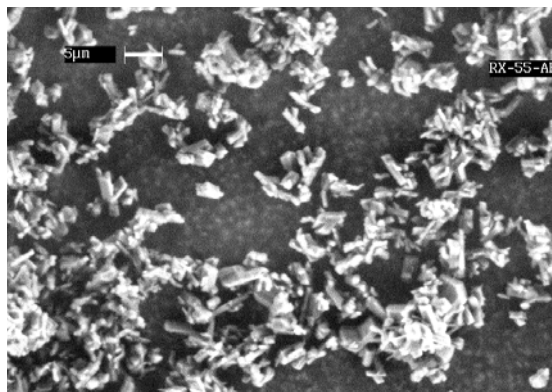
LLM-105 type	Preparation method	Morphology (average size, micron)	Drop hammer DH50, cm
0	Unrecrystallized (original)	(80)	115-120
1	Slow recrystallization from DMSO/water	Sharp needles (60)	105
2	Crash precipitates from DMSO/cold water	Small particles (2)	60
3	Crash precipitates from Butyrolactone/xylene solution	Rounded granules and small fines (40 + 2)	55
4	Type 1 materials subjected to milling for 22 hrs	Fractured granules (2)	80

*Formulation* – Several 25 g-quantities of plastic-bonded explosives containing LLM-105 and a binder (Viton A or Kel-F) were formulated using a Cramer mixer. These formulations are labeled as RX-55-XX. Typically, a 10% Viton A in acetone solution was prepared in a mixer bowl. An appropriate amount of LLM-105 material was added to this solution. The composite was mixed initially by hand and then remotely under vacuum in the mixer. The slurry was continually mixed with heating until most of the solvent was removed (~ 30 minutes). The powder was recovered into a petri dish and dried under vacuum at  $55 \pm 5^{\circ}\text{C}$  for 2 days or until a constant weight was observed. Table 2 lists RX-55 formulations that were prepared under this work.

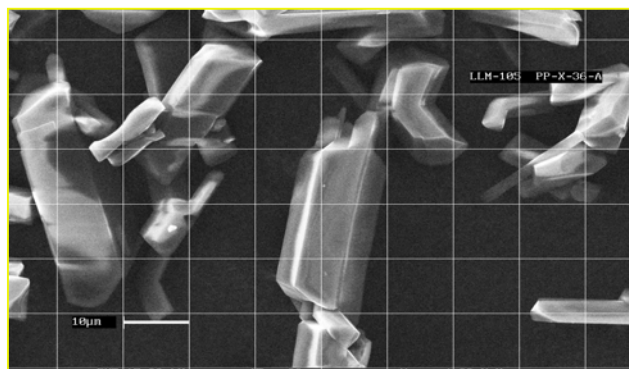
*Pressing* – Small pellets (12.7 mm diameter x 4 mm thick) were pressed for Floret experiments (test description provided below). The pressing conditions were at 200 MPa and  $105^{\circ}\text{C}$  for 3 cycles with a 5-minute dwell per cycle under low vacuum (400 mtorr or less). The highest



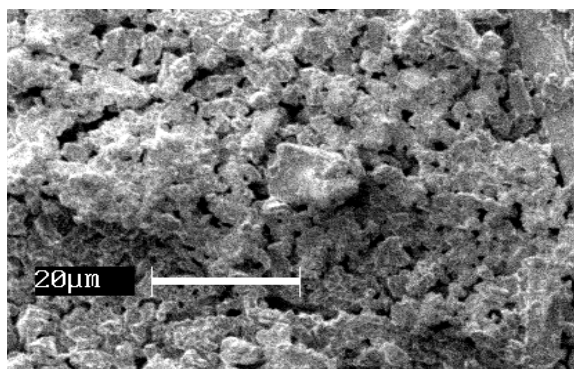
Type 1- LLM-105 particles were recrystallized DMSO/water soln



Type 2 – particles recrystallized via crash precipitation from cold DMSO/water



Type 3 – Recrystallized fr. Butyrolactone/xylene



Type 4 – Type 1 grounded for 22 hours

Figure 2. Scanning electron micrographs of several LLM-105 particles. The scale in all micrographs is approximately the same for comparison

density achieved for each material under these conditions is included in Table 2. Working specimens at densities lower than these values were prepared by varying the amount of powder.

*Detonation spreading spot-size tests* – A modified Floret test (3) was used to screen and rank the performance of these materials and other common explosives. This modified test (3, 4), measures the spot size imparted on a copper witness plate as a result of the detonating sample. The cavity depth and its shape are useful semi-quantitative measures of the pellet energy and its detonation-spreading (divergence) characteristics, respectively. Figure 4 shows a schematic of the Floret assembly. This set-up was adapted from the LLNL's Tiny plate experiment (5) and contained several modifications. The two main differences were the use of an Al flyer plate in our test

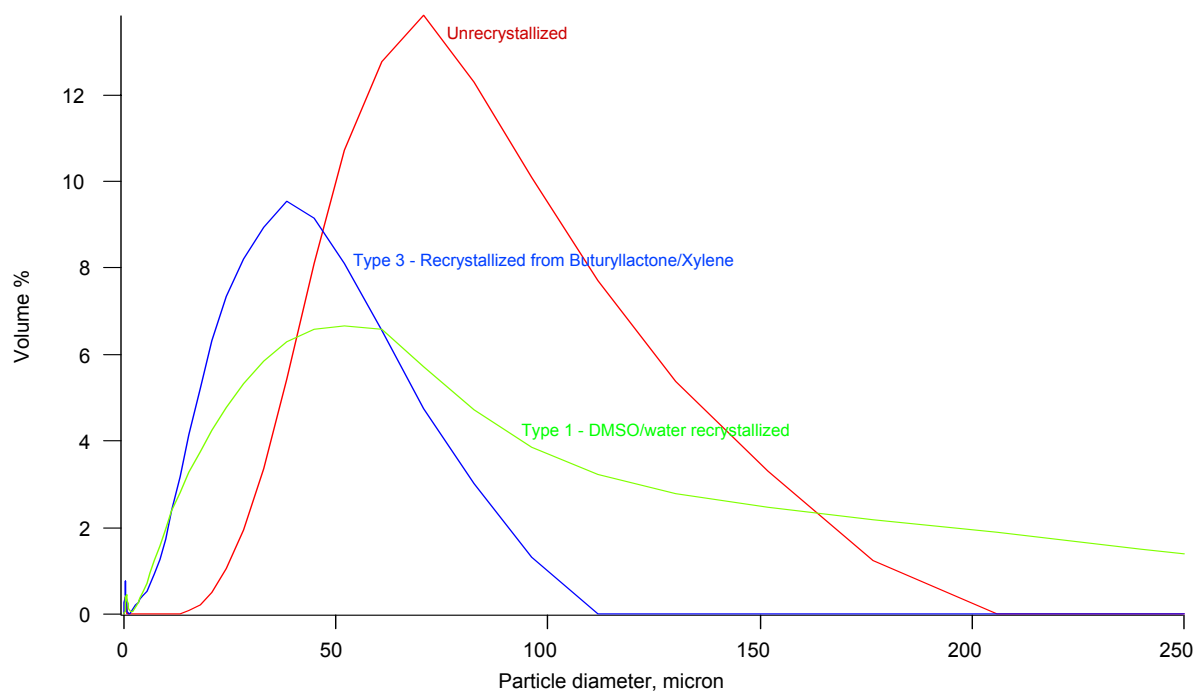


Figure 3. The particle size distribution for several types of LLM-105

Table 2. List of several formulations containing UF-TATB, LLM-105 and a binder

Formulation	LLM-105 type	Weight percent, %				TMD, g/cc	Max. density pressed*	
		UF-TATB	LLM-105	Viton A	Kel-F		g/cc	% TMD
UF-TATB		100				1.938	1.857	96
LLM-105			100			1.913	Not pressable	
RX-55-AA	1		95	5		1.910		
RX-55-AB	1		92.4		7.6	1.921	1.865	97
RX-55-AE	2		97.5	2.5		1.911	1.676	88
RX-55-AE2	3		97.5	2.5		1.911	1.76	92
RX-55-AF	2	75	22.5	2.5		1.929	1.857	96

\* Based on pressing of Floret specimens under conditions specified in text

(versus a stainless steel one in Lee et al's experiment) and stainless steel spacer/housing components held together by thick plates with nuts and bolts. The latter introduces additional confinement to the system.

The test involves initiating a 12.7-mm diameter x 4-mm thick IHE pellet using a 5.1-mm diameter x 0.125-mm thick Aluminum flyer plate. A LX-16 pellet (density =  $1.70 \pm 0.01$  g/cc) drives the flyer across a 1.83 mm gap before impacting the acceptor specimen. The LX-16 pellet was detonated with an exploding foil initiator. A copper witness plate (50.8 mm x 50.8-mm square x 25.4 mm thick) placed on the opposite surface, records the output of the detonating pellet. The various components were stacked together with 50.8-mm stainless steel discs as spacer or housing components. The stacks were held together with six 10 mm-diameter nut and bolts. Tests were done at ambient temperature and at - 54°C.

*Dent profile analysis* – The dent shape profile across the center was read using a profilometer (Cordax 1808-MZ DCC MEA, Sheffield Measurement) which was programmed to take reading every 25.4  $\mu\text{m}$  along the horizontal scan through the center of the dent. Minor corrections were made to account for the small tilt and slight offset in the cavity profile record associated with each test. The volumes of the cavities were determined by numerical integration using an Excel spreadsheet.

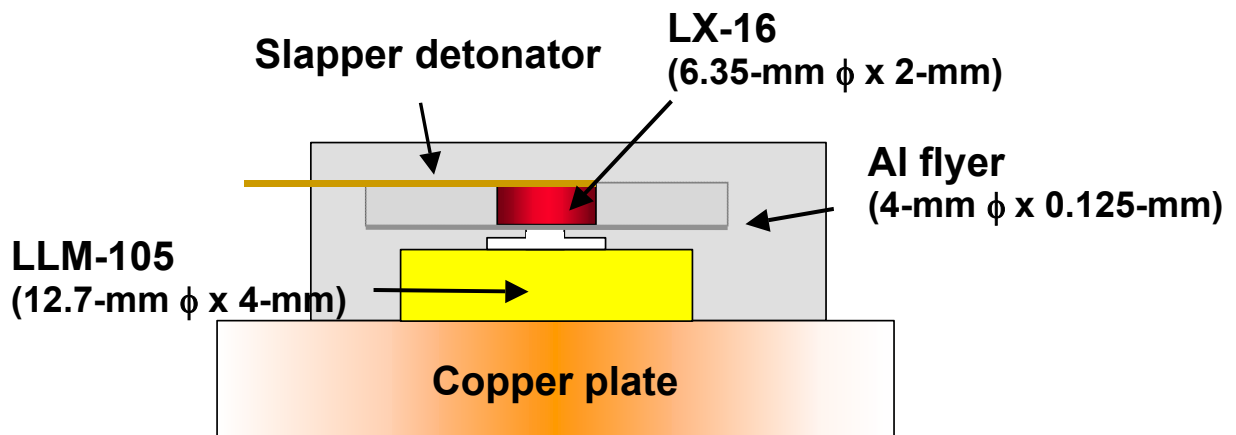


Figure 4: A schematic of a modified Floret test assembly at LLNL. Stainless steel holding plates with nut and bolts components are not shown



## Results and Discussion

The LLM-105 particle morphology and chemical purity are dependent on its synthetic and processing history. Development activities to date have yielded several materials with a range of particle sizes and morphologies. The initial selection criteria for an optimum particle was based on purity, ease and efficiency of synthesis and processing characteristics. Table 1 lists five types of LLM-105 particles that are in this study. All morphologies are thermally stable and are insensitive to spark and friction (data not included here). The impact insensitivity is sensitive to particle size and morphology. The relationship of particle morphology and its safety characteristics is not well understood and is the subject of on-going investigation.

The energy output and divergence of formulations containing LLM-105 particles and a binder were primarily evaluated using the Floret experiments. The spot-size associated with each material is compared to those from a series of UF-TATB at different densities. The latter results have been demonstrated to yield different dent sizes which are useful as a qualitative performance scale. The effects of density, binder type and composition and flyer size on the pellet energy output and divergence were also studied in this work.

*UF-TATB performance at different densities* - A series of Floret experiments with UF-TATB at various densities between 1.69 and 1.83 g/cc was completed to establish a baseline ranking of the spot size profiles. A blank test was also conducted where a Teflon pellet replaced the UF-TATB sample.

The profiles through the center of the cavities formed as the results of the detonating pellets are shown in Figure 5. The cavities are very symmetric as suggested from the representative profiles shown. The sharp tips in the profiles are artifacts due to the 10-fold compression of the x-axis relative to the y-axis. When the axes are scaled geometrically, the tip of the cavity is fairly spherical in shape. Dent diameters in region in contact with the pellet are generally found to be larger than the diameter of the sample (depicted as the yellow disc in Figure 5).

The dent depths and widths reflect a strong dependence of density on the energy output and divergence behavior. While the density range (1.690-1.835 g/cc) for these specimens represents

only a 10% difference in energy content, the resulting cavity volumes varies by as much as 350%, suggesting a significant difference in energy output. UF-TATB at 1.761 g/cc yielded the deepest dent. The pellet at this density completely detonated and no residue was found after the test. Test with 1.83 g/cc pellet showed much smaller cavity. Yellow powder was observed after the experiment, indicative of a partial detonation. The difference in the cavity sizes is attributed to the different divergence behavior in these samples. Good divergence in lower density materials (e.g., 1.761 g/cc) facilitated lateral spreading of the detonation wave and allowed most or all of the pellet to react. On the contrary, poor divergence in the densest pellet (1.835 g/cc) resulted in less lateral spreading, produced less energy and, therefore, a smaller spot size. Interestingly, the larger spot size for this densest pellet relative to that from a blank (Teflon) indicated that some of the UF-TATB materials were detonated under these conditions.

This semi-quantitative relationship between the cavity volumes and density provides a useful scale for ranking the relative divergence behavior of new formulations. Such information can provide quick feedback to chemists and processing engineers on the effects of experimental variables on the material performance.

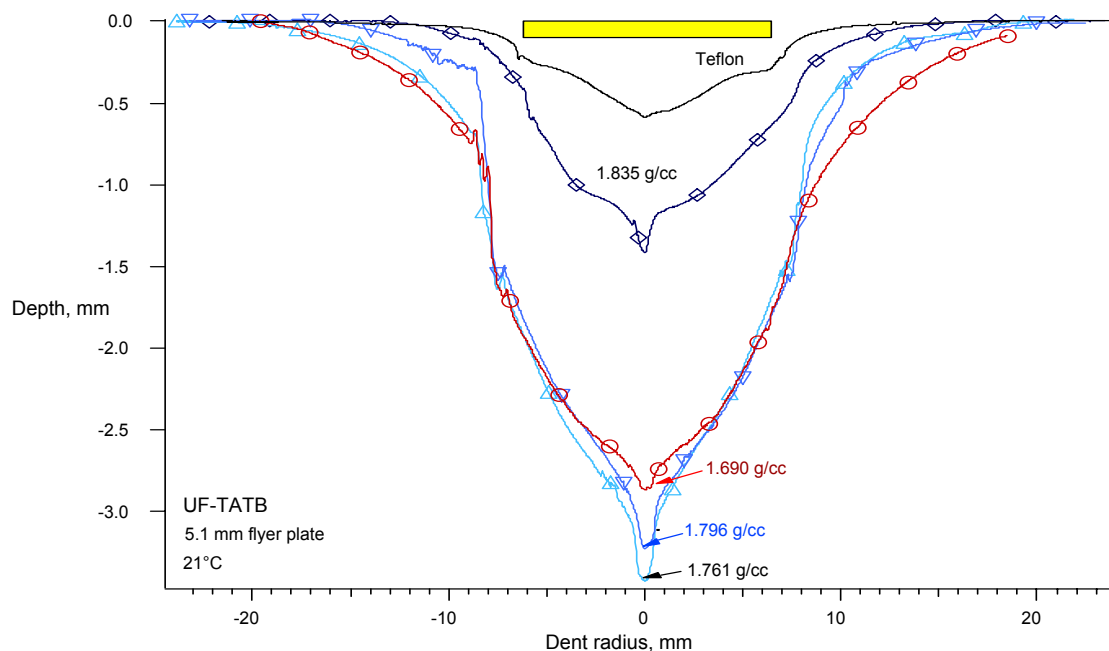


Figure 5. Dent profiles for UF-TATB pellets at various densities

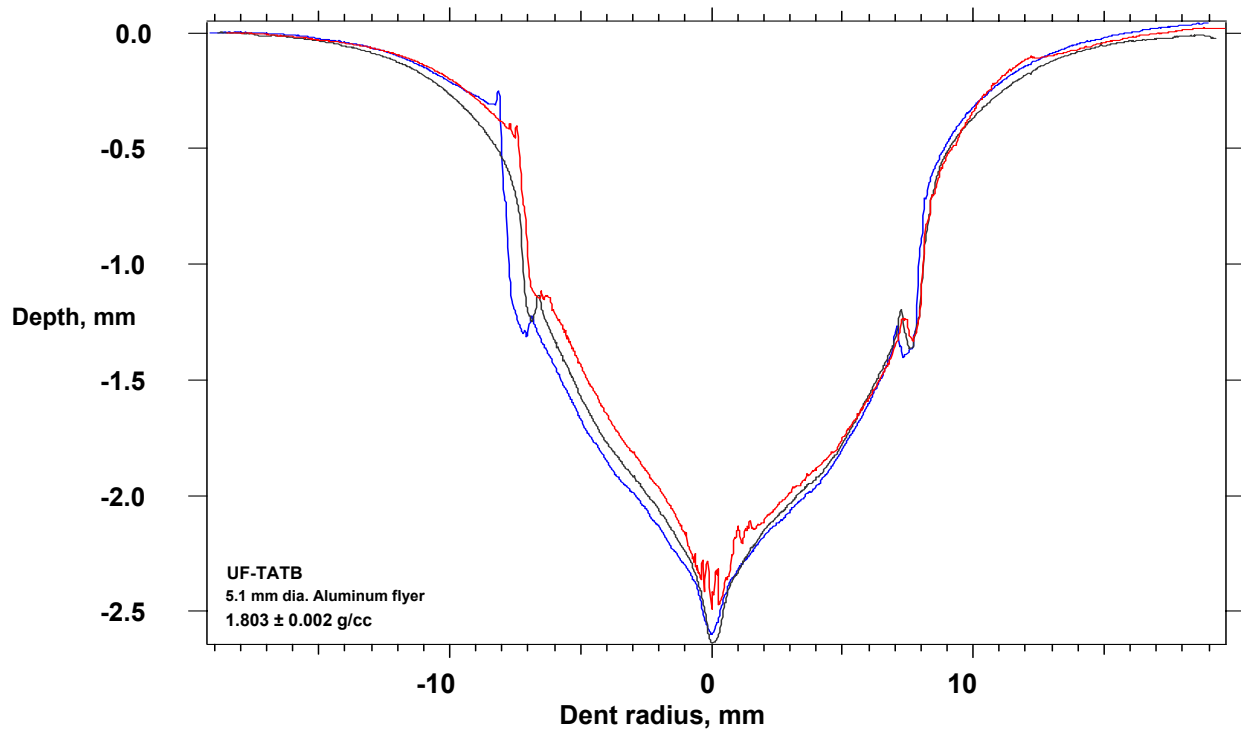


Figure 6. Reproducibility tests for several RX-55-AE2 samples under identical conditions

The results here are consistent with the trend observed by Lee et al. (4). However, the cavities in our tests are about twice as deep. The larger spot sizes are attributed to higher confinement in our experiments as well as other experimental factors (different flyer material and a larger gap.) Also, the UF-TATB materials are different in both works.

*Floret test reproducibility* – The reproducibility of the cavity sizes was evaluated in three Floret tests conducted under identical conditions. The results are shown in Figure 6. The shape and general features of the cavity are very reproducible. The integrated volumes are reproducible to about 5%.

*Effects of binder type and composition* - Figure 7 compares the performance of four formulations containing various LLM-105 concentrations and particle morphologies with that of UF-TATB. All composites containing LLM-105 show profiles that are deeper and wider than that of the optimum UF-TATB pellet (at 1.796 g/cc).

RX-55-AB (92.5 wt% LLM-105, 7.5 wt% Kel-F), formulated like LX-17, can be pressed to high density (see table 2) and still produced more energy output than that of UF-TATB. RX-55-AE with 97.5 wt% LLM-105 (type 2) and 2.5 wt% Viton-A binder showed the largest profile. RX-55-AE2 formulation, consisting of another type of LLM-105 (type 3) with the same amount of binder, showed slightly less energy than that containing the type 2 molecule but still superior to that for UF-TATB. RX-55-AF (75 wt% UF-TATB, 22.5 wt% LLM-105, 2.5 wt% Viton A) showed UF-TATB-like profile but higher energy output.

*Effects of temperature on LLM-105 performance* - The better divergence observed with RX-55-AE2 formulation was clearly exhibited in experiments conducted under cold temperatures (i.e., -54°C). This was contrasted to that for UF-TATB (see Figure 8). A smaller flyer plate (3.8 mm diameter) was used to initiate the RX-55-AE2 pellets. The profile of cold RX-55-AE2 is significantly deeper and broader than that for UF-TATB. Also, the temperature effects on RX-55-AE2 is much less pronounced than that seen for UF-TATB. The results clearly demonstrate

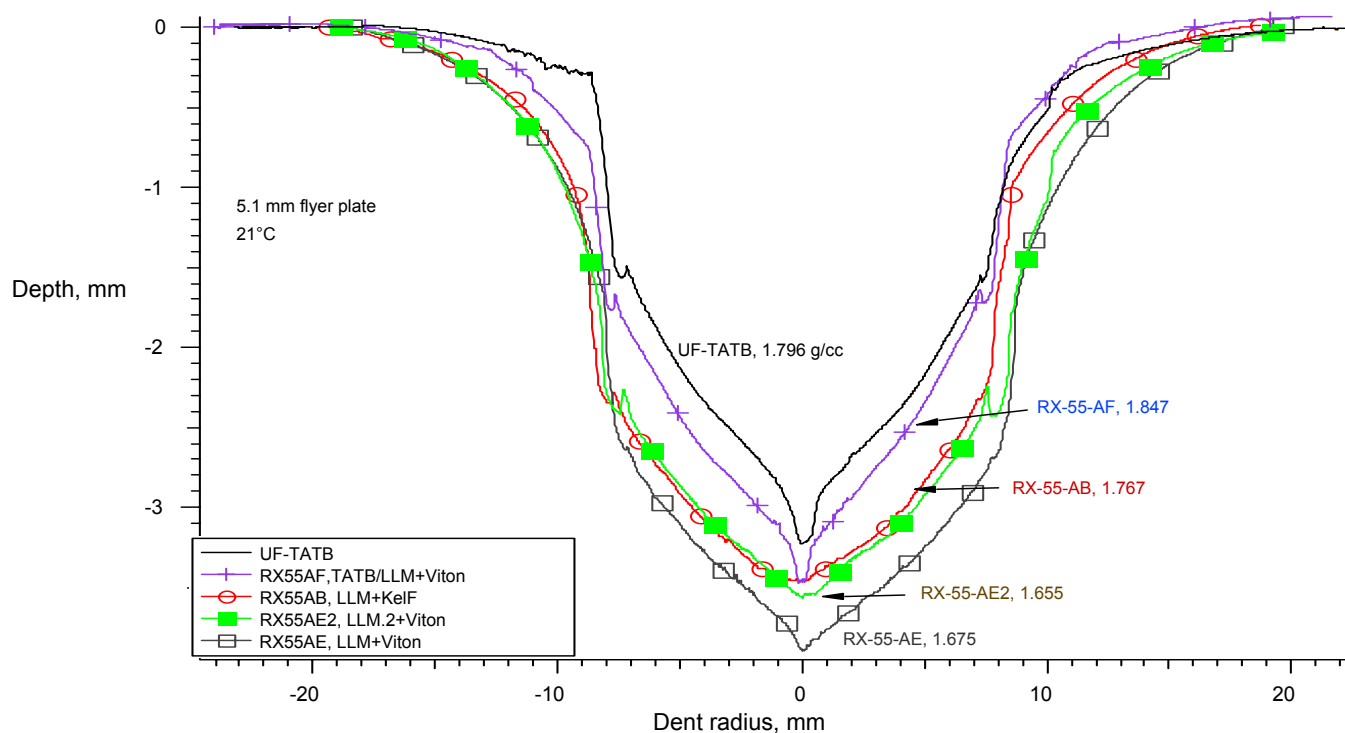


Figure 7. Dent profiles showing better output from several formulations of LLM-105 when compared with that of UF-TATB

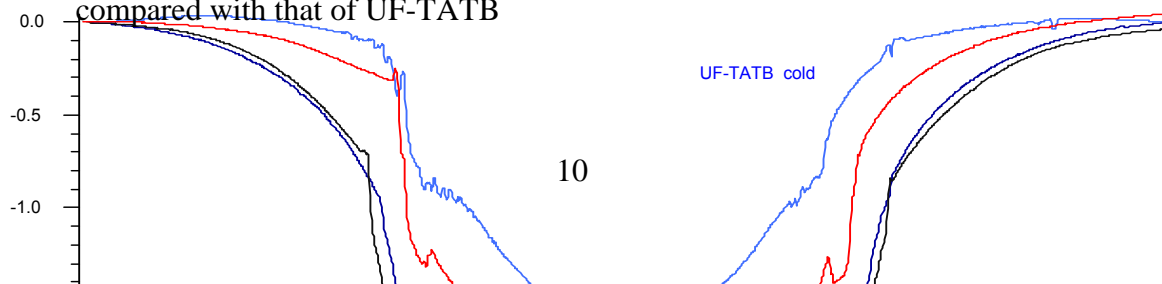


Figure 8. Comparison of dent profiles of UF-TATB and RX-55-AE2 for Floret tests at ambient conditions and  $-54^{\circ}\text{C}$ .

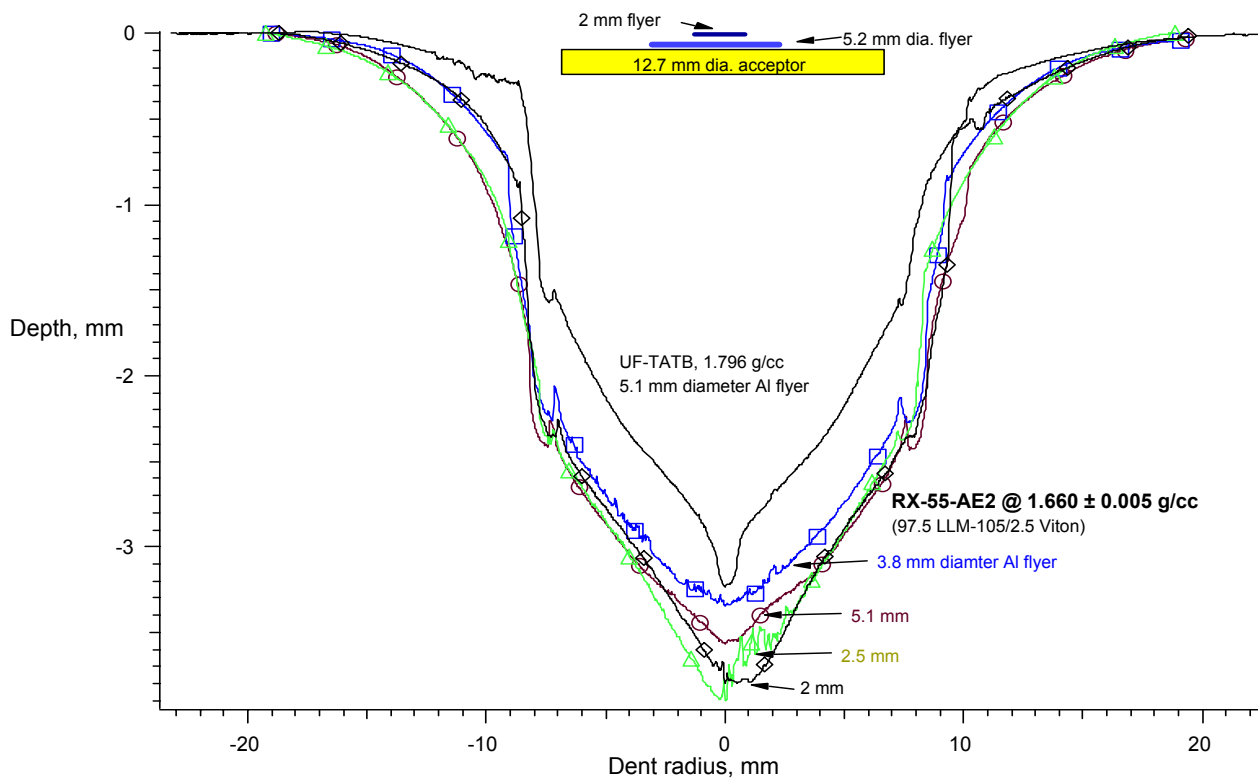


Figure 9. Effects of flyer plate diameter on dent profiles of RX-55-AE2. Floret tests conducted at ambient conditions.

that the detonation-spreading behavior of this LLM-105 formulation was superior to that of UF-TATB at cold temperature.

*Effects of flyer size on LLM-105 initiation* – The effects of using a smaller flyer plate for initiating LLM-105 composites are studied and the results are illustrated in Figure 9. Aluminum flyer plates with diameters between 2 to 5.1 mm were used to initiate RX-55-AE2 pellets at similar densities ( $1.660 \pm 0.005$  g/cc.) Full detonation was observed for all tests. The profiles for all tests are deeper and broader than that for UF-TATB. Divergence in these RX-55-AE2 pellets is good and the resulting lateral spreading consumes most or all of the pellets since no yellowish residue was observed. The relationship of the depth of the spot size and the flyer diameter is not clear at this time. Additional experiments will be required to elucidate this effect. The results, nevertheless, demonstrated that a much smaller flyer can be used to initiate formulations containing LLM-105. The failure diameter of this formulation is clearly less than 2 mm.

## **Summary**

Small-scale safety tests, pressing studies and Floret experiments were conducted to characterize several formulations containing, UF-TATB, LLM-105 and another binder. The results demonstrate that LLM-105 is a promising high-performance insensitive high explosive material. Several LLM-105 formulations developed as booster materials show higher energy and better divergence than UF-TATB. Even-higher performance can be expected with improved particle morphology and a selection of a higher density formulation.

## **Acknowledgement**

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